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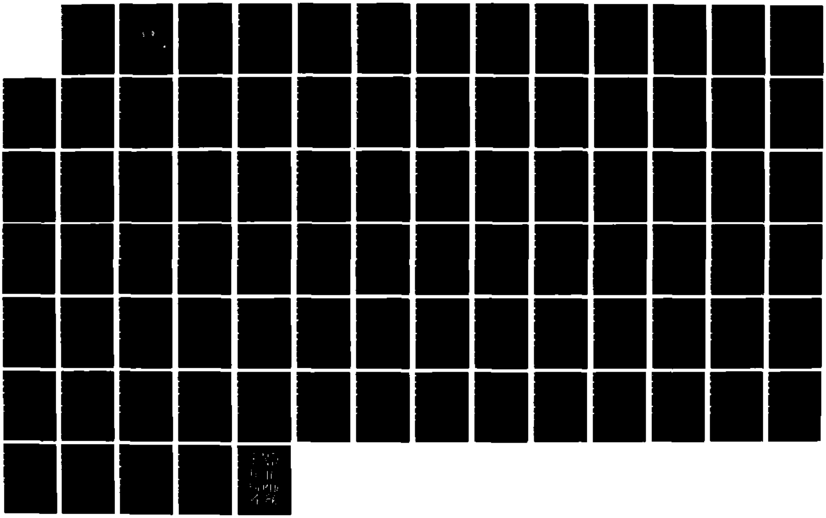

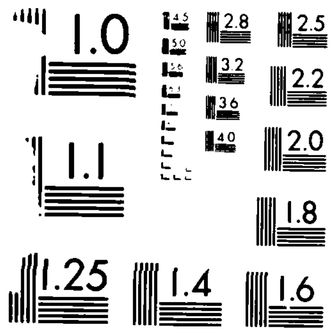

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Classical Derivation of Nonlinear Susceptibilities for the 32 Crystal Classes in the Harmonic Oscillator Approximation

by Clyde A. Morrison
Mary S. Tobin

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER HDL-TR-2078	2. GOVT ACCESSION NO. ADA164536	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Classical Derivation of Nonlinear Susceptibilities for the 32 Crystal Classes in the Harmonic Oscillator Approximation		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Clyde A. Morrison Mary S. Tobin		8. CONTRACT OR GRANT NUMBER(s) PRON: 1F4R0007011FA9
9. PERFORMING ORGANIZATION NAME AND ADDRESS Harry Diamond Laboratories 2800 Powder Mill Road Adelphi, MD 20783-1197		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Ele: 61101A DA Project: 1L161101A91A
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Laboratory Command 2800 Powder Mill Road Adelphi, MD 20783-1145		12. REPORT DATE January 1986
		13. NUMBER OF PAGES 86
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

HDL Project: A10436
AMS Code: 6111091A0011

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nonlinear optics
Harmonic oscillator model

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

New applications relating to optical information processing, optical limiting, and frequency-agile laser systems have produced a resurgence of interest in nonlinear optical materials. In this work, we extend the classical anharmonic analysis to describe the nonlinear optical properties of the 32 crystal classes. We derive expressions for and relationships between the nonlinear susceptibility tensor elements in terms of the anharmonic force constants according to the crystal class symmetry. We show that all the susceptibilities thus derived ($\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$) obey the Kleinman conditions. Finally, we discuss the possible application of these results, coupled with a point-charge model, for estimating the nonlinear force constants, in the prediction of potential new nonlinear materials.

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1. INTRODUCTION

There has been considerable recent interest in the use of nonlinear optical materials for all-optical image and signal processing.[1,2] The development of new tunable-frequency (agile) lasers has also created demands for new nonlinear materials for optical harmonic generation, which by now is a conventional nonlinear optical technique.[3] These devices or techniques are ultimately all limited by materials. In this report, we develop a theoretical technique using a three-dimensional anharmonic oscillator model to derive the nonlinear susceptibilities of crystalline materials. This technique may have application in predicting potential new nonlinear materials. We derive expressions for the nonlinear susceptibility tensor elements in terms of the anharmonic force constants and derive relationships between the tensor elements according to the symmetry of the 32 crystal classes.

This report is organized as follows. In section 2, some relevant background material on nonlinear optics is given. (The reader is referred elsewhere[4-9] for a more in-depth review.) We describe our approach in section 3. In section 4, the anharmonic oscillator model is briefly discussed. The method of construction of the anharmonic oscillator terms in the potential energy is described in section 5, with specific examples. The solution of the Lorentz force equation, containing anharmonic terms, is given in section 6. The solutions give rise to $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$. We, however, present the nonlinear results in terms of Miller's δ. The final results for all the crystal classes are collected in the appendix, where the invariant polynomials, resultant potential, and Miller's δ are listed for each crystal class. The results automatically obey the Kleinman conditions.[10]

2. BACKGROUND

Large optical electric (**E**) fields produce a nonlinear response in the medium. The resultant effects are describable by the induced polarization

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[1] A. M. Glass, Materials for Optical Information Processing, Science 226 (1984), 657.

[2] A. R. Tanguay, Materials Requirement for Optical Processing and Computing Devices, Opt. Engineering 24 (1985), 002.

[3] R. S. Adhav, Materials for Optical Harmonic Generation, Laser Focus 19 (1983), 73.

[4] R. W. Minck, R. W. Terhune, and C. C. Wang, Nonlinear Optics, Appl. Opt. 5 (1966), 1596.

[5] R. W. Terhune and P. D. Maker, Nonlinear Optics, in Advances in Lasers, Vol II, ed by A. K. Levine, M. Dekker, Inc., New York (1968), pp 295-372.

[6] S. Singh, Non-linear Optical Materials, in Handbook of Lasers, ed. by R. J. Pressley, The Chemical Rubber Co. (1971).

[7] C. Flytzanis, Theory of Nonlinear Optical Susceptibilities, in Quantum Electronics: A Treatise, Vol. 1, Nonlinear Optics, Part A, ed. by H. Robin and C. L. Tang, Academic Press, New York (1975).

[8] R. L. Byer, Parametric Oscillators and Nonlinear Materials, in Nonlinear Optics, ed. by P. G. Harper and B. S. Wherrett, Academic Press, New York (1977).

[9] F. Zernike and J. E. Midwinter, Applied Nonlinear Optics, John Wiley, New York (1973).

[10] D. A. Kleinman, Nonlinear Dielectric Polarization in Optical Media, Phys. Rev. 126 (1962), 1977.

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$$\mathbf{P} = \chi^{(1)}\mathbf{E} + \chi^{(2)}\mathbf{E}^2 + \chi^{(3)}\mathbf{E}^3 + \ldots \tag{1}$$

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second-order and third-order nonlinear optical susceptibilities. $\chi^{(1)}$ which we will refer to simply as χ is the linear susceptibility. For isotropic material, χ is related to the refractive index n by

$$\chi = (n^2 - 1)/4\pi \tag{2}$$

in esu. For anisotropic materials, χ becomes a tensor. We assume that the susceptibilities and indices of refraction are measured along the principal optic axes so that $\chi_{ii} = (n_i - 1)/4\pi$. We consider light of a single frequency ω and limit the discussion to the nonlinear processes of second-harmonic and third-harmonic generation. For now we consider second-harmonic generation. The second-order polarization at 2ω is usually written

$$P_i^{2\omega} = d_{ijk}^{2\omega} E_j^{\omega} E_k^{\omega} \quad , \tag{3}$$

where i,j,k refer to the coordinates x,y,z = 1,2,3 and we assume summation over repeated indices. The $d_{ijk}^{2\omega}$ are the second-harmonic-generation coefficients which are the components of a third rank tensor where $d_{ijk}^{2\omega} = d_{ikj}^{2\omega}$. Because of the symmetry of j and k, it is customary to contract the jk suffix to ℓ, where ℓ = 1 to 6 replaces jk = 11, 22, 33, 23 (or 32), 13 (or 31), 12 (or 21), respectively. Experimentalists generally report measurements in terms of $d^{2\omega}$ rather than $\chi^{(2)}$; however, these two tensors are simply related to each other by constants according to the particular tensor element:

$$\chi_{i\ell}^{(2)} = d_{i\ell}^{2\omega} \text{ for } \ell \leq 3 \text{ and } \chi_{i\ell}^{(2)} = 2d_{i\ell}^{2\omega} \text{ for } \ell \geq 4 \quad . \tag{4}$$

In terms of the contracted $d_{i\ell}^{2\omega}$'s, one can express $P^{2\omega}$ as

$$\begin{bmatrix} P_x^{2\omega} \\ P_y^{2\omega} \\ P_z^{2\omega} \end{bmatrix} = \begin{bmatrix} d_{11}^{2\omega} & d_{12}^{2\omega} & d_{13}^{2\omega} & d_{14}^{2\omega} & d_{15}^{2\omega} & d_{16}^{2\omega} \\ d_{21}^{2\omega} & d_{22}^{2\omega} & d_{23}^{2\omega} & d_{24}^{2\omega} & d_{25}^{2\omega} & d_{26}^{2\omega} \\ c_{31}^{2\omega} & d_{32}^{2\omega} & d_{33}^{2\omega} & d_{34}^{2\omega} & d_{35}^{2\omega} & d_{36}^{2\omega} \end{bmatrix} \begin{bmatrix} E_x^2 \\ E_y^2 \\ E_z^2 \\ 2E_yE_z \\ 2E_xE_z \\ 2E_xE_y \end{bmatrix} \tag{5}$$

The symmetry properties of the crystal classes are used to determine the nonvanishing components and relationships between elements of the $d^{2\omega}$ tensor[6,8,11,12] and, similarly, for the $d^{3\omega}$ tensor,[13] as summarized by Flytzanis.[7] An immediate consequence of symmetry is that the second-order nonlinear coefficients vanish for centrosymmetric media. In addition to crystal symmetry, there is a symmetry relation based on a conjecture by Kleinman[10] that, in a lossless medium, $\chi^{(2)}_{ijk}$ is symmetric under any permutation of the indices. Kleinman's condition for a general $d^{2\omega}_{i\ell}$ matrix is

$$\begin{bmatrix} 11 & 12 & 13 & 14 & 15 & 16 \\ 21 & 22 & 23 & 24 & 25 & 26 \\ 31 & 32 & 33 & 34 & 35 & 36 \end{bmatrix} = \begin{bmatrix} 11 & 12 & 13 & 14 & 15 & 16 \\ 16 & 22 & 23 & 24 & 14 & 12 \\ 15 & 24 & 33 & 23 & 13 & 14 \end{bmatrix} , \qquad (6)$$

where we have only written the subscripts $i\ell$.

In 1964, Miller[14] reported that the quantity

$$\delta^{2\omega}_{ijk} = \frac{d^{2\omega}_{ijk}}{\chi_{ii}(2\omega)\chi_{jj}(\omega)\chi_{kk}(\omega)} \qquad (7)$$

is nearly a constant for the materials that he investigated. This result, known as Miller's rule, has had use in predicting good nonlinear materials. The rule indicates that materials with large linear susceptibilities should have large second-order nonlinearities. (Notice that the $\delta^{2\omega}$ is defined in terms of the $d^{2\omega}$ given by eq (4); otherwise factors of 2 appear in the $\delta^{2\omega}_{i\ell}$ for $\ell \geq 3$.)

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[6] S. Singh, Non-linear Optical Materials, in Handbook of Lasers, ed. by R. J. Pressley, The Chemical Rubber Co. (1971).

[7] C. Flytzanis, Theory of Nonlinear Optical Susceptibilities, in Quantum Electronics: A Treatise, Vol. 1, Nonlinear Optics, Part A, ed. by H. Robin and C. L. Tang, Academic Press, New York (1975).

[8] R. L. Byer, Parametric Oscillators and Nonlinear Materials, in Nonlinear Optics, ed. by P. G. Harper and B. S. Wherrett, Academic Press, New York (1977).

[10] D. A. Kleinman, Nonlinear Dielectric Polarization in Optical Media, Phys. Rev. 126 (1962), 1977.

[11] R. Bechmann, R. F. S. Hearman, and S. K. Kurtz, Elastic, Piezoelectric, Piezooptic, Electrooptic Constants, and Nonlinear Dielectric Susceptibilities of Crystals, Vol. 2, in Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology, New Series Group III: Crystal and Solid State Physics, ed. by K. H. Hellwege and A. M. Hellwege, Springer Verlag, Berlin (1969), pp 167-209.

[12] R. R. Birss, Property Tensors in Magnetic Crystal Classes, Proc. Phys. Soc. 79 (1962), 946.

[13] P. N. Butcher, Nonlinear Optical Phenomena, Ohio State University Engineering Bulletin, Columbus, Ohio (1965).

[14] R. C. Miller, Optical Second Harmonic Generation in Piezoelectric Crystals, Appl. Phys. Lett. 5 (1965), 17.

To our knowledge, Lax et al[15] were the first to use the one-dimensional anharmonic oscillator model, incorporated into a band model, to describe the nonlinear properties of a solid. Bloembergen[16] used the one-dimensional anharmonic oscillator model to estimate the one-dimensional nonlinear force constant by considering the magnitude of the atomic forces within a cell. Garrett and Robinson[17] extended arguments involving the one-dimensional anharmonic oscillator to make order-of-magnitude calculations of Miller's δ. Yariv[18] provides a concise review of this work. Adler,[19] in his discussion of nonlinear optical frequency polarization in a dielectric, introduces constants $\chi_{\phi\beta\delta}$ in the force equations of a three-dimensional harmonic oscillator model; however, he does not investigate the properties of $\chi_{\phi\beta\delta}$ for the different crystal classes. Robinson[20] discusses the three-dimensional harmonic oscillator model but does not investigate the consequence of making the potential energy invariant for the particular crystal classes. He does, however, point out the relationship of the constants in the potential if the potential satisfies Laplace's equation. We have not found any detailed application of the anharmonic oscillator model in three dimensions to nonlinear optics.

3. APPROACH

In this report we introduce anharmonic terms into the potential energy of a three-dimensional oscillator model such that each term is invariant under the operations of the point group of a particular crystal class.[21]* The 32 point groups are listed in table 1. Invariant polynomials of order two are sufficient for the linear susceptibility, χ; third-degree polynomials are required for $\chi^{(2)}$ and fourth-degree polynomials are used for $\chi^{(3)}$. For the lowest symmetry crystal class (triclinic, C_1 (1)) the number of independent polynomials, N_n, of degree n, is given by the number of terms in the expansion of $(x + y + z)^n$. For a given n, there are $N_n = (n + 1)(n + 2)/2$ polynomials. For the lower crystal classes (triclinic, monoclinic, and orthorhombic--1 through 8),† we assume, with no loss of generality (but a great deal less algebra), that the coordinate system x,y,z is parallel to the principal optic axes of the crystal. Using the potential energy in the Lorentz force equa-

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[15] B. Lax, J. G. Mavroides, and D. F. Edwards, Nonlinear Interband and Plasma Effects in Solids, Phys. Rev. Lett. 8 (1962), 166.

[16] N. V. Bloembergen, Nonlinear Optics: A Lecture Note and Reprint Volume, Benjamin, New York (1965).

[17] C. G. B. Garrett and F. N. H. Robinson, Miller's Phenomenological Rule for Computing Nonlinear Susceptibilities, IEEE J. Quantum Electron. QE-2 (1966), 328.

[18] A. Yariv, *Quantum Electronics*, 2nd ed., Wiley, New York (1975).

[19] E. Adler, Nonlinear Optical Frequency Polarization in a Dielectric, Phys. Rev. A134 (1964), 728.

[20] F. N. H. Robinson, Nonlinear Optical Coefficients, Bell Sys. Tech. J. 46 (1967), 913.

[21] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two point Groups, MIT, Cambridge, MA (1963).

*In our references to a particular crystal class we give the Schoenflies symbol first, followed by the international symbol in parentheses.

†The ordering of the crystal classes is as given by Koster et al (ref 21).

TABLE 1. CLASSIFICATION OF THE 32 POINT GROUPS

System	Unit cell	Point group number	Symmetry	Number of symmetry elements
Triclinic	$a \neq b \neq c$	1	C_1 (1)	1
	$\alpha \neq \beta \neq \gamma$	2	C_i ($\bar{1}$)	2
Monoclinic	$a \neq b \neq c$	3	C_2 (2)	2
	$\alpha = \gamma = \pi/2 \neq \beta$	4	C_s (m)	2
		5	C_{2h} (2/m)	4
Orthorhombic	$a \neq b \neq c$	6	D_2 (222)	4
	$\alpha = \beta = \gamma = \pi/2$	7	C_{2v} (mm2)	4
		8	D_{2h} (mmm)	8
Tetragonal	$a = b \neq c$	9	C_4 (4)	4
	$\alpha = \beta = \gamma = \pi/2$	10	S_4 ($\bar{4}$)	4
		11	C_{4h} (4/m)	8
		12	D_4 (422)	8
		13	C_{4v} (4mm)	8
		14	D_{2d} ($\bar{4}$2m)	8
		15	D_{4h} (4/mmm)	16
Rhombohedral (trigonal)	$a = b = c$	16	C_3 (3)	3
	$\alpha = \beta = \gamma < 2\pi/3 \neq \pi/2$	17	C_{3i}, S_6 ($\bar{3}$)	6
		18	D_3 (32)	6
		19	C_{3v} (3m)	6
		20	D_{3d} ($\bar{3}$m)	12
Hexagonal	$a = b \neq c$	21	C_6 (6)	6
	$\alpha = \beta = \pi/2,\ \gamma = 2\pi/3$	22	C_{3h} ($\bar{6}$)	6
		23	C_{6h} (6/m)	12
		24	D_6 (622)	12
		25	C_{6v} (6mm)	12
		26	D_{3h} ($\bar{6}$m2)	12
		27	D_{6h} (6/mmm)	24
Cubic	$a = b = c$	28	T (23)	12
	$\alpha = \beta = \gamma = \pi/2$	29	T_h (m3)	24
		30	O (432)	24
		31	T_d ($\bar{4}$3m)	24
		32	O_h (m3m)	48

tion, the susceptibilities χ, $\chi^{(2)}$, and $\chi^{(3)}$ are derived for the 32 crystal classes. We show that all the susceptibilities thus derived obey the Kleinman's conditions[10] given in equation (6). In fact, for any crystal class, the number of independent third- or fourth-degree polynomials is equal to the number of independent $d_{i\ell}^{2\omega}$ or $d_{i\ell}^{3\omega}$, so that each $d_{i\ell}$ corresponds to a particular constant in the anharmonic potential. No attempt is made here to derive the constants in the potential energy from more fundamental theory. That is, each constant in the potential energy allowed by symmetry is assumed phenomenological and, at this point, is determined by fitting experimental data. In particular, the constants in the quadratic terms of the potential energy, the harmonic oscillator, can be determined from the measured index of refraction at various wavelengths by using the Sellmeyer or Sellmeier equations.[22,23]

The $\delta_{ijk}^{2\omega}$ of Miller's rule are given simply in terms of the constants (β_i) of the potential energy $U^{(n)}$ with n = 3 so that these constants can be related to experimental data. The extension of Miller's rule to $\delta_{ijk\ell}^{3\omega}$ is straightforward for those crystal classes where $\delta_{ijk}^{2\omega} = 0$ ($\beta_i = 0$), in which case the $\delta_{ijk\ell}^{3\omega}$ are simply related to the constants (γ_i) of the fourth-degree terms in potential energy. The extension of Miller's rule for $\delta_{ijk\ell}^{3\omega}$ to those crystal classes where $\delta_{ijk}^{2\omega} \neq 0$, which is generally not simple, is also given.

4. ANHARMONIC OSCILLATOR MODEL

We assume that the nonlinear polarization is electronic in origin and start with the Lorentz model which has been used to describe the linear response of the electrons in a solid to an electric field.[24] In this model, the equation of motion for an electron is

$$m\ddot{\mathbf{r}} = -e\mathbf{E} - \nabla U \quad , \tag{8}$$

where m is the mass of the electron, e is the electronic charge, $\mathbf{r}$ is the position of the electron, $\mathbf{E}$ is the applied electric field seen by the electron, and U is the potential of the electron in the solid. We will ignore losses which could be included by a damping term $-m\Gamma\dot{\mathbf{r}}$ on the right-hand side of equation (8) where Γ is the damping constant. In an isotropic solid, the potential for a harmonic oscillator model is chosen as

$$U = \frac{1}{2} m\omega_0^2(x^2 + y^2 + z^2) \quad , \tag{9}$$

where ω_0 is a representative resonance frequency of the solid. If the potential given in equation (9) is used in equation (8), we obtain

$$m\ddot{\mathbf{r}} = -e\mathbf{E} - m\omega_0^2\mathbf{r} \quad , \tag{10}$$

[10] D. A. Kleinman, Nonlinear Dielectric Polarization in Optical Media, Phys. Rev. 126 (1962), 1977.

[22] M. Born and E. Wolf, Principles of Optics, Pergamon Press, New York (1964), p 97.

[23] C. F. J. Bottcher and P. Bordewijk, Theory of Electric Polarization, Vol II, Elsevier, New York (1978), p 288.

[24] J. D. Jackson, Classical Electrodynamics, 2nd Edition, McGraw-Hill, New York (1975), p 285.

and if a time dependence of cos ωt is chosen for **E**, we obtain

$$\mathbf{r} = \frac{-\frac{e}{m}\mathbf{E}}{\omega_0^2 - \omega^2} = \frac{-\mathbf{E}}{D(\omega)} \quad , \tag{11}$$

where $D(\omega) = m(\omega_0^2 - \omega^2)/e$. The polarization, **P**, is related to the displacement, **r**, by

$$\mathbf{P} = -Ne\mathbf{r} \quad , \tag{12}$$

where N is the number of electrons per unit volume that contribute to **P**. Substituting (11) into (12) and using $\mathbf{P} = \chi\mathbf{E}$, we obtain

$$\chi(\omega) = \frac{Ne}{D(\omega)} \quad . \tag{13}$$

For large displacement from the electronic equilibrium position, the anharmonicity of the electron oscillators must be taken into account as done by Bloembergen[16] for the one-dimensional anharmonic oscillator model. In the lowest order nonlinear approximation, the anharmonicity is introduced through a potential energy term proportional to the cube of the displacement--$[-(1/3)\beta x^3]$--where we use β for the nonlinear force constant. This term gives rise to second-harmonic generation through the nonlinear polarization term

$$P_x^{2\omega} = \chi^{(2)} E_x(\omega) E_x(\omega) \quad , \tag{14}$$

where the second-order nonlinear susceptibility can be shown to be

$$\chi^{(2)} = \frac{N\left(\frac{e^3}{m^2}\right)\beta}{D^2(\omega)D(2\omega)} \tag{15}$$

(equation (1-14) of Bloembergen[16]).

5. ANHARMONIC POTENTIAL

5.1 Invariant Polynomials

By far the most difficult part of the work reported here is the construction of the anharmonic terms in the potential energy. Unfortunately, we have not found a universal method of constructing these polynomials but have resorted to a number of devices to achieve our goal. The most useful technique is what might be called the replacement method. That is, for a given operator, O, of a group we have

[16] N. V. Bloembergen, Nonlinear Optics: A Lecture Note and Reprint Volume, Benjamin, New York (1965).

$$O(x,y,z) \rightarrow \text{(some permutation of } x,y,z) \tag{16}$$

for each operation O of the group. For example, the operator C_4, which represents a 90° rotation about z, can be written

$$C_4(x,y,z) \rightarrow (y,-x,z) \quad . \tag{17}$$

The 32 point groups are listed in table 1. For the operations, we follow the conventions of Koster et al,[21] where an explicit description of each of the operations of the point groups is given. Each polynomial and combination of polynomials can be tested for invariance, and proper combinations can be selected. This method works quite well for all the groups except for those with a threefold or sixfold rotation. For other conventions, such as IRE, the reader can extend the methods used here in a straightforward manner.

It is convenient to list explicitly the polynomials of various degree in tabular form. The polynomials of order 2, 3, and 4 are given in table 2, which also identifies the labels of the coefficients of the polynomials of order 3 and 4, β and γ, respectively.

5.2 Examples

5.1.2 Crystal Class 10, S_4

Crystal class S_4 is a cyclic group containing the single generator S_4 which gives

$$\begin{aligned} S_4(x,y,z) &= (y,-x,-z) \quad , \\ S_4^2(x,y,z) &= (-x,-y,+z) \quad , \\ S_4^3(x,y,z) &= (-y,x,-z) \quad . \end{aligned} \tag{18}$$

We see immediately that z^2 is invariant and $x^2 + y^2$ is also invariant.

Using table 2a, we can now write the term in the potential, $U^{(2)}$ as

$$U^{(2)} = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 \quad . \tag{19}$$

The m_x and m_z are introduced as "effective masses" which can be determined by fitting the linear susceptibilities to the measured indices of refraction.[22,23]

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[21] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups, MIT, Cambridge, MA (1963).

[22] M. Born and E. Wolf, Principles of Optics, Pergamon Press, New York (1964), p 97.

[23] C. F. J. Bottcher and P. Bordewijk, Theory of Electric Polarization, Vol II, Elsevier, New York (1978), p 288.

TABLE 2. POLYNOMIALS OF ORDER N, $Q_i^{(n)}$, AND MULTIPLICATIVE CONSTANTS IN POTENTIAL ENERGY $U^{(n)}$

(a) n = 2 where $U^{(2)} = \sum_i \alpha_i Q_i^{(2)}$

α_i	$Q_i^{(2)}$
$m_x\omega_x^2$	$\frac{1}{2}x^2$
$m_y\omega_y^2$	$\frac{1}{2}y^2$
$m_z\omega_z^2$	$\frac{1}{2}z^2$

(b) n = 3 where $U^{(3)} = \sum_i \beta_i Q_i^{(3)}$

β_i	$Q_i^{(3)}$
β_1	$\frac{1}{3}x^3$
β_2	$\frac{1}{3}y^3$
β_3	$\frac{1}{3}z^3$
β_4	x^2y
β_5	x^2z
β_6	y^2x
β_7	y^2z
β_8	z^2x
β_9	z^2y
β_0	$2xyz$

(c) n = 4 where $U^{(4)} = \sum_i \gamma_i Q_i^{(4)}$

i	$Q_i^{(4)}$
γ_1	$\frac{1}{4}x^4$
γ_2	$\frac{1}{4}y^4$
γ_3	$\frac{1}{4}z^4$
γ_4	x^3y
γ_5	x^3z
γ_6	y^3x
γ_7	y^3z
γ_8	z^3x
γ_9	z^3y
γ_{10}	$\frac{3}{2}x^2y^2$
γ_{11}	$\frac{3}{2}x^2z^2$
γ_{12}	$\frac{3}{2}y^2z^2$
γ_{13}	$3x^2yz$
γ_{14}	$3y^2xz$
γ_{15}	$3z^2xy$

We find that xyz and $z(x^2 - y^2)$ are the only invariant polynomials of order three. Using table 2b we have $\beta_7 = -\beta_5$ and consequently,

$$U^{(3)} = \beta_5(x^2 - y^2)z + 2\beta_0 xyz \tag{20}$$

and all other $\beta_i = 0$.

For the fourth-degree terms in the potential energy, we see immediately that z^4 is invariant. Since $x^2 + y^2$ is invariant, $(x^2 + y^2)^2$ is also; however, $x^4 + y^4$ is invariant, so we additionally have x^2y^2 and $z^2(x^2 + y^2)$. The last remaining fourth-degree polynomial is $xy(x^2 - y^2)$. Thus, the invariant polynomials of order 4 are

$$x^4 + y^4, \quad z^4, \quad xy(x^2 - y^2), \quad x^2y^2, \quad z^2(x^2 + y^2) \quad . \tag{21}$$

From table 2c we have

$$\begin{aligned} &\gamma_2 = \gamma_1, \quad \gamma_6 = -\gamma_4, \quad \gamma_{12} = \gamma_{11}, \quad \text{and} \\ &\gamma_5 = \gamma_7 = \gamma_8 = \gamma_9 = \gamma_{13} = \gamma_{14} = \gamma_{15} = 0 \end{aligned} \tag{22}$$

with the resulting potential energy

$$\begin{aligned} U^{(4)} = &\frac{1}{4}\gamma_1(x^4 + y^4) + \frac{1}{4}\gamma_3 z^4 + \gamma_4 xy(x^2 - y^2) \\ &+ \frac{3}{2}\gamma_{10}x^2y^2 + \frac{3}{2}\gamma_{11}z^2(x^2 + y^2) \quad . \end{aligned} \tag{23}$$

The results given in equations (19), (20), and (23) express the potential energy expanded through polynomials of fourth order.

5.2.2 Crystal Class 16, C_3

The crystal class C_3 is a cyclic group containing the single generator C_3 which gives

$$\begin{aligned} &C_3(x,y,z) \to (x\cos\phi + y\sin\phi, -x\sin\phi + y\cos\phi, z) \\ &C_3^2(x,y,z) \to (x\cos 2\phi + y\sin 2\phi, -x\sin 2\phi + y\cos 2\phi, z) \end{aligned} \tag{24}$$

with $\phi = 2\pi/3$. Since z is invariant, any power of z is invariant. Note that $x^2 + y^2$ is invariant, so that the potential of second order can be written (table 2a)

$$U^{(2)} = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 \quad . \tag{25}$$

For the third-degree polynomials, we have immediately z^3 and $z(x^2 + y^2)$. To obtain the other polynomials using the replacement method, the amount of

algebra is prohibitive, and we resort to methods used in the theory of paramagnetic ions in crystals.[25-27] From these references and using Koster et al[21] (page 53), we find that the spherical harmonics Y_{30} and $Y_{3,\pm 3}$ are invariant under the operation C_3. Tables of the spherical harmonics in Cartesian form are given by Ballhausen[25] and Prather.[27] Leaving out the normalization constants, they are

$$
\begin{aligned}
Y_{30} &\sim 2z^3 - 3z(x^2 + y^2) \quad , \\
\text{Real } Y_{33} &\sim x^3 - 3xy^2 \quad , \\
\text{Imaginary } Y_{33} &\sim 3x^2y - y^3 \quad .
\end{aligned}
\tag{26}
$$

We already have found the two polynomials z^3 and $z(x^2 + y^2)$ of Y_{30}, but the two contained in Y_{33} are new. No other combinations can be found. We now have all the polynomials of third order: z^3, $x^3 - 3xy^2$, $y^3 - 3x^2y$, and $z(x^2 + y^2)$. From table 2b we have $\beta_6 = -\beta_1$, $\beta_4 = -\beta_2$, $\beta_7 = \beta_5$, and $\beta_8 = \beta_9 = \beta_0 = 0$. Thus, we have

$$
U^{(3)} = \frac{1}{3}\beta_1(x^3 - 3xy^2) + \frac{1}{3}\beta_2(y^3 - 3x^2y) + \frac{1}{3}\beta_3 z^3 + \beta_5 z(x^2 + y^2) \tag{27}
$$

for the potential energy of third order.

The terms of fourth order in the potential are obtained using the previous methods and are

$$
(x^2 + y^2)^2 \ , \quad z^4 \ , \quad z(x^3 - 3xy^2) \ , \quad z(y^3 - 3x^2y) \ , \quad \text{and } z^2(x^2 + y^2) \quad . \tag{28}
$$

These results can be checked by examining the expressions for Y_{40} and Y_{43} (real and imaginary parts)[25,27] which if done shows that there are no more polynomials of fourth order. The constants in the potential energy involving the fourth-order polynomials given in equation (28) can be determined using table 2c:

$$
\begin{gathered}
\gamma_2 = \gamma_1 \ , \quad \gamma_{10} = \frac{1}{3}\gamma_1 \ , \quad \gamma_{14} = -\gamma_5 \ , \quad \gamma_{13} = -\gamma_7 \ , \quad \gamma_{12} = \gamma_{11} \quad , \\
\text{and} \\
\gamma_4 = \gamma_6 = \gamma_8 = \gamma_9 = \gamma_{15} = 0 \quad .
\end{gathered}
\tag{29}
$$

The fourth-order potential energy $U^{(4)}$ is then given by

---

[21] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups, MIT, Cambridge, MA (1963).

[25] C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York (1962).

[26] M. Timkin, Group Theory and Quantum Mechanics, McGraw-Hill, New York (1964).

[27] J. L. Prather, Atomic Energy Levels in Crystals, National Bureau of Standards, Monograph 19, U.S. Government Printing Office (1961), p 5.

$$U^{(4)} = \frac{1}{4}\gamma_1(x^2 + y^2)^2 + \frac{1}{4}\gamma_3 z^4 + \gamma_5 z(x^3 - 3xy^2)$$
$$+ \gamma_7 z(y^3 - 3x^2y) + \frac{3}{2}\gamma_{11} z^2(x^2 + y^2) \quad . \tag{30}$$

The invariant polynomials for all the 32 crystal classes can be constructed using the above techniques. In appendix A, the invariant polynomials and potential energy expanded through order 4 are explicitly written for each crystal class. The results are given in summary form for $U^{(3)}$ in table 3 and for $U^{(4)}$ in table 4.

6. EQUATION OF MOTION AND SOLUTION

To simplify the solution of the equation of motion, equation (8), we assume that the material is lossless in the region of interest. This reduces the algebra considerably. We use a perturbation technique which is essentially an expansion of the displacements in powers of the electric field. To illustrate the technique we shall set up the equations and their solution for the C_1 crystal class. Since the C_1 crystal class has no symmetry, the results for any crystal class of higher symmetry can be obtained by using the methods of the previous section along with the results of tables 3 and 4.

From appendix A the potential energy for the crystal class C_1 is given as

$$U = \frac{1}{2} m_x\omega_x^2 x^2 + \frac{1}{2} m_y\omega_y^2 y^2 + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{3}\beta_1 x^3 + \frac{1}{3}\beta_2 y^3 + \frac{1}{3}\beta_3 z^3 + \beta_4 x^2 y$$
$$+ \beta_5 x^2 z + \beta_6 xy^2 + \beta_7 y^2 z + \beta_8 xz^2 + \beta_9 yz^2 + 2\beta_0 xyz + \frac{1}{4}\gamma_1 x^4$$
$$+ \frac{1}{4}\gamma_2 y^4 + \frac{1}{4}\gamma_3 z^4 + \gamma_4 x^3 y + \gamma_5 x^3 z + \gamma_6 xy^3 + \gamma_7 y^3 z + \gamma_8 xz^3 \tag{31}$$
$$+ \gamma_9 yz^3 + \frac{3}{2}\gamma_{10} x^2y^2 + \frac{3}{2}\gamma_{11} x^2z^2 + \frac{3}{2}\gamma_{12} y^2z^2 + 3\gamma_{13} x^2yz$$
$$+ 3\gamma_{14} xy^2z + 3\gamma_{15} xyz^2 \quad .$$

The components of the equation of motion are obtained by using the above expression in equation (8) to give

$$m_x\ddot{x} = -eE_x - m_x\omega_x^2 x - \beta_1 x^2 - 2\beta_4 xy - 2\beta_5 xz - \beta_6 y^2 - \beta_8 z^2 - 2\beta_0 yz$$
$$- \gamma_1 x^3 - 3\gamma_4 x^2 y - 3\gamma_5 x^2 z - \gamma_6 y^3 - \gamma_8 z^3 - 3\gamma_{10} xy^2 \tag{32}$$
$$- 3\gamma_{11} xz^2 - 6\gamma_{13} xyz - 3\gamma_{14} y^2 z - 3\gamma_{15} yz^2$$

with similar equations for y and z.

We assume that the field $E_x \to E_x\delta$ and that $x = x_1\delta + x_2\delta^2 + x_3\delta^3$, with a similar expression for the other two components, and where δ is such that at the end we set $\delta = 1$.

TABLE 3. $U^{(3)}$ FOR ALL CRYSTAL CLASSES[a]

No.	Symmetry	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8	β_9	β_0
1	C_1	1	1	1	1	1	1	1	1	1	1
2	C_i	0	0	0	0	0	0	0	0	0	0
3	C_2	0	0	1	0	1	0	1	0	0	1
4	C_s	1	1	0	1	0	1	0	1	1	0
5	C_{2h}	0	0	0	0	0	0	0	0	0	0
6	D_2	0	0	0	0	0	0	0	0	0	1
7	C_{2v}	0	0	1	0	1	0	1	0	0	0
8	D_{2h}	0	0	0	0	0	0	0	0	0	0
9	C_4	0	0	1	0	1	0	β_5	0	0	0
10	S_4	0	0	0	0	1	0	$-\beta_5$	0	0	1
11	C_{4h}	0	0	0	0	0	0	0	0	0	0
12	D_4	0	0	0	0	0	0	0	0	0	0
13	C_{4v}	0	0	1	0	1	0	β_5	0	0	0
14	D_{2d}	0	0	0	0	0	0	0	0	0	1
15	D_{4h}	0	0	0	0	0	0	0	0	0	0
16	C_3	1	1	1	$-\beta_2$	1	$-\beta_1$	β_5	0	0	0
17	C_{3i}	0	0	0	0	0	0	0	0	0	0
18	D_3	0	1	0	$-\beta_2$	0	0	0	0	0	0
19	C_{3v}	1	0	1	0	1	$-\beta_1$	β_5	0	0	0
20	D_{3d}	0	0	0	0	0	0	0	0	0	0
21	C_6	0	0	1	0	1	0	β_5	0	0	0
22	C_{3h}	1	1	0	$-\beta_2$	0	$-\beta_1$	0	0	0	0
23	C_{6h}	0	0	0	0	0	0	0	0	0	0
24	D_6	0	0	0	0	0	0	0	0	0	0
25	C_{6v}	0	0	1	0	1	0	β_5	0	0	0
26	D_{3h}	0	1	0	$-\beta_2$	0	0	0	0	0	0
27	D_{6h}	0	0	0	0	0	0	0	0	0	0
28	T	0	0	0	0	0	0	0	0	0	1
29	T_h	0	0	0	0	0	0	0	0	0	0
30	O	0	0	0	0	0	0	0	0	0	0
31	T_d	0	0	0	0	0	0	0	0	0	1
32	O_h	0	0	0	0	0	0	0	0	0	0

[a] *A "1" or "0" in the table represents the multiplier of β_i. Other entries (e.g., "$-\beta_5$") represent the replacement term for β_i.*

TABLE 4. $U^{(4)}$ FOR ALL CRYSTAL CLASSES[a]

No.	Symmetry	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6	γ_7	γ_8	γ_9	γ_{10}	γ_{11}	γ_{12}	γ_{13}	γ_{14}	γ_{15}
1	C_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	C_i	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
3	C_2	1	1	1	1	0	1	0	0	0	1	1	1	0	0	1
4	C_s	1	1	1	1	0	1	0	0	0	1	1	1	0	0	1
5	C_{2h}	1	1	1	1	0	1	0	0	0	1	1	1	0	0	1
6	D_2	1	1	1	0	0	0	0	0	0	1	1	1	0	0	0
7	C_{2v}	1	1	1	0	0	0	0	0	0	1	1	1	0	0	0
8	D_{2h}	1	1	1	0	0	0	0	0	0	1	1	1	0	0	0
9	C_4	1	γ_1	1	1	0	$-\gamma_4$	0	0	0	1	1	γ_{11}	0	0	0
10	S_4	1	γ_1	1	1	0	$-\gamma_4$	0	0	0	1	1	γ_{11}	0	0	0
11	C_{4h}	1	γ_1	1	1	0	$-\gamma_4$	0	0	0	1	1	γ_{11}	0	0	0
12	D_4	1	γ_1	1	0	0	0	0	0	0	1	1	γ_{11}	0	0	0
13	C_{4v}	1	γ_1	1	0	0	0	0	0	0	1	1	γ_{11}	0	0	0
14	D_{2d}	1	γ_1	1	0	0	0	0	0	0	1	1	γ_{11}	0	0	0
15	D_{4h}	1	γ_1	1	0	0	0	0	0	0	1	1	γ_{11}	0	0	0
16	C_3	1	γ_1	1	0	1	0	1	0	0	$\gamma_1/3$	1	γ_{11}	$-\gamma_7$	$-\gamma_5$	0
17	C_{3i}	1	γ_1	1	0	1	0	1	0	0	$\gamma_1/3$	1	γ_{11}	$-\gamma_7$	$-\gamma_5$	0
18	D_3	1	γ_1	1	0	1	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	$-\gamma_5$	0
19	C_{3v}	1	γ_1	1	0	1	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	$-\gamma_5$	0
20	D_{3d}	1	γ_1	1	0	1	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	$-\gamma_5$	0
21	C_6	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
22	C_{3h}	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
23	C_{6h}	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
24	D_6	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
25	C_{6v}	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
26	D_{3h}	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
27	D_{6h}	1	γ_1	1	0	0	0	0	0	0	$\gamma_1/3$	1	γ_{11}	0	0	0
28	T	1	γ_1	γ_1	0	0	0	0	0	0	1	γ_{10}	γ_{10}	0	0	0
29	T_h	1	γ_1	γ_1	0	0	0	0	0	0	1	γ_{10}	γ_{10}	0	0	0
30	O	1	γ_1	γ_1	0	0	0	0	0	0	1	γ_{10}	γ_{10}	0	0	0
31	T_d	1	γ_1	γ_1	0	0	0	0	0	0	1	γ_{10}	γ_{10}	0	0	0
32	O_h	1	γ_1	γ_1	0	0	0	0	0	0	1	γ_{10}	γ_{10}	0	0	0

[a] *A "1" or "0" in the table represents the multiplier of γ_i. Other entries (e.g., "$-\gamma_5$") represent the replacement of terms for γ_i.*

Using these expressions in equation (32) and equating powers of δ, we obtain

$$
\begin{aligned}
m_x\ddot{x}_1 &= -eE_x - m_x\omega_x^2 x_1 \quad , \\
m_y\ddot{y}_1 &= -eE_y - m_y\omega_y^2 y_1 \quad , \qquad (33) \\
m_z\ddot{z}_1 &= -eE_z - m_z\omega_z^2 z_1 \quad ,
\end{aligned}
$$

for the terms of first order in δ,

$$m_x\ddot{x}_2 = -m_x\omega_x^2 x_2 - \beta_1 x_1^2 - 2\beta_4 x_1 y_1 - 2\beta_5 x_1 z_1 - \beta_6 y_1^2 - \beta_8 z_1^2 - 2\beta_0 y_1 z_1 \qquad (34)$$

for the terms of second order in δ, and

$$
\begin{aligned}
m_x\ddot{x}_3 = &-m_x\omega_x^2 x_3 - 2\beta_1 x_1 x_2 - 2\beta_4(x_1 y_2 + x_2 y_1) - 2\beta_5(x_1 z_2 + x_2 z_1) \\
&- 2\beta_6 y_1 y_2 - 2\beta_8 z_1 z_2 - 2\beta_0(y_1 z_2 + y_2 z_1) - \gamma_1 x_1^3 - 3\gamma_4 x_1^2 y_1 \\
&- 3\gamma_5 x_1^2 z_1 - \gamma_6 y_1^3 - \gamma_8 z_1^3 - 3\gamma_{10} x_1 y_1^2 - 3\gamma_{11} x_1 z_1^2 \qquad (35) \\
&- 6\gamma_{13} x_1 y_1 z_1 - 3\gamma_{14} y_1^2 z_1 - 3\gamma_{15} y_1 z_1^2
\end{aligned}
$$

for the terms of third order in δ where, for simplicity, we have written only the x-components.

The results given in equations (33), (34), and (35) are sufficient to obtain the susceptibilities χ, $\chi^{(2)}$, and $\chi^{(3)}$. We make use of equation (12) generalized to

$$P_x^{n\omega} = -Nex_n \qquad (36)$$

with $n = 1, 2, 3$ and similar expressions for y and z.

We start by solving the first-order equations given in equation (33). Since we are ignoring losses, we can assume that any time-dependent quantity varies as $\cos(\omega t - \phi)$, so that the solutions are

$$
\begin{aligned}
x_1 &= -E_x/D_x \quad , \\
y_1 &= -E_y/D_y \quad , \qquad (37) \\
z_1 &= -E_z/D_z \quad ,
\end{aligned}
$$

and consequently, we obtain the components of the linear susceptibility tensor

$$\chi_{ii} = Ne/D_i \quad , \qquad (38)$$

where $D_i = D_i(\omega) = m_i(\omega_i^2 - \omega^2)/e$. We will give the argument of D_i explicitly only when it is 2ω or 3ω.

Using the result of equation (37) in equation (34), we have

$$x_2 = -\frac{\beta_1 E_x^2}{eD_x(2\omega)D_x^2} - \frac{\beta_6 E_y^2}{eD_x(2\omega)D_y^2} - \frac{\beta_8 E_z^2}{eD_x(2\omega)D_z^2} - \frac{2\beta_4 E_x E_y}{eD_x(2\omega)D_x D_y} \tag{39}$$

$$- \frac{2\beta_5 E_x E_z}{eD_x(2\omega)D_x D_z} - \frac{2\beta_0 E_y E_z}{eD_x(2\omega)D_y D_z} \quad .$$

We can rewrite equation (5) as

$$P_x^{2\omega} = \sum_{\ell=1}^{6} d_{i\ell}^{2\omega} V_\ell \tag{40}$$

where V_ℓ are given in terms of the electric-field components according to equation (5). Using equations (36), (38), and (40), we obtain

$$d_{11}^{2\omega} = g\beta_1 \chi_{xx}(2\omega)\chi_{xx}\chi_{xx} \quad ,$$

$$d_{12}^{2\omega} = g\beta_6 \chi_{xx}(2\omega)\chi_{yy}\chi_{yy} \quad , \tag{41}$$

$$d_{13}^{2\omega} = g\beta_8 \chi_{xx}(2\omega)\chi_{zz}\chi_{zz} \quad , \text{etc},$$

where $g = 1/N^2e^3$. Comparing the results given in equation (41) with equation (7), we have

$$\delta_{11}^{2\omega} = \beta_1 g \ , \quad \delta_{12}^{2\omega} = \beta_6 g \ , \quad \delta_{13}^{3\omega} = \beta_8 g \ , \quad \delta_{14}^{2\omega} = \beta_0 g \ , \quad \delta_{15}^{2\omega} = \beta_5 g \ ,$$

and

$$\delta_{16}^{2\omega} = \beta_4 g \quad .$$

Similarly, the solutions for y_2 and z_2 give rise to $\delta_{2\ell}^{2\omega}$ and $\delta_{3\ell}^{2\omega}$. We can write the resultant $\delta_{i\ell}^{2\omega}$ in matrix form as

$$\delta^{2\omega} = \frac{1}{N^2e^3}\begin{bmatrix} \beta_1 & \beta_6 & \beta_8 & \beta_0 & \beta_5 & \beta_4 \\ \beta_4 & \beta_2 & \beta_9 & \beta_7 & \beta_0 & \beta_6 \\ \beta_5 & \beta_7 & \beta_3 & \beta_9 & \beta_8 & \beta_0 \end{bmatrix} . \tag{42}$$

Note that $\delta^{2\omega}$ satisfies the Kleinman conditions given in equation (6).

The solutions for the third-order displacement x_3 are obtained by using the results of (37) and (39) in (35). It can be seen by inspection of equation (35) that we can express the solution as $x_3 = x_3' + x_3''$ where $x_3' \to 0$ as $\beta_i \to 0$ and $x_3'' \to 0$ as $\gamma_i \to 0$. For simplicity of demonstration, we will write only the portion of x_3 containing the γ terms, which is

$$
\begin{aligned}
eD_x(3\omega)x_3'' = {} & \frac{\gamma_1 E_x^3}{D_x^3} + \frac{\gamma_6 E_y^3}{D_y^3} + \frac{\gamma_8 E_z^3}{D_z^3} + \frac{3\gamma_4 E_x^2 E_y}{D_x^2 D_y} \\
& + \frac{3\gamma_{14} E_y^2 E_z}{D_y^2 D_z} + \frac{3\gamma_{11} E_z^2 E_x}{D_x D_z^2} + \frac{3\gamma_5 E_x^2 E_z}{D_x^2 D_z} \qquad (43) \\
& + \frac{3\gamma_{10} E_x E_y^2}{D_x D_y^2} + \frac{3\gamma_{15} E_y E_z^2}{D_y^2 D_z} + \frac{6\gamma_{13} E_x E_y E_z}{D_x D_y D_z} \quad .
\end{aligned}
$$

The solution for x_3 gives rise to $P_x^{3\omega} = -Nex_3$.

The third-order polarization can be expressed as $P_i^{3\omega} = \chi_{ijk\ell} E_j E_k E_\ell$; however, in analogy to the case for $P^{2\omega}$, we use the reduced basis for $P^{3\omega}$. Following the convention of Maker and Terhune,[28] we write $P_i^{3\omega} = \chi_{im}^{(3)} U_m$ where subscripts $jk\ell$ are replaced by m and $E_j E_k E_\ell$ is replaced by U_m, as shown in table 5. Again in analogy with second-harmonic generation, we can express

$$P_i^{3\omega} = d_{im}^{3\omega} Q_m \quad , \qquad (44)$$

where $d_{im}^{3\omega}$ are the third-harmonic generation coefficients and

$$
\begin{aligned}
Q_m &= U_m \text{ for } 1 \le m \le 3 \quad , \\
Q_m &= 3U_m \text{ for } 3 \le m \le 9 \quad , \qquad (45) \\
Q_0 &= 6U_0 \text{ for } m = 0 \quad .
\end{aligned}
$$

TABLE 5. RELATIONSHIP BETWEEN $P_i^{3\omega} = \chi_{ijk\ell}^{(3)} E_j E_k E_\ell$ and $\chi_{im}^{(3)} U_m$

$jk\ell$:	111	222	333	112	223	331	113	122	233	123
m:	1	2	3	4	5	6	7	8	9	0
U_m:	E_x^3	E_y^3	E_z^3	$E_x^2E_y$	$E_y^2E_z$	$E_z^2E_x$	$E_x^2E_z$	$E_y^2E_x$	$E_z^2E_y$	$E_xE_yE_z$

[28] P. D. Maker and R. W. Terhune, Study of Optical Effects due to an Induced Polarization Third Order in the Electric Field Strength, Phys. Rev. 137A (1965), 801.

Using the results given in table 5 along with equations (44) and (45), we can write the Kleinman conditions for $d_{im}^{3\omega}$ as

$$\begin{bmatrix} 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & 10 \\ 21 & 22 & 23 & 24 & 25 & 26 & 27 & 28 & 29 & 20 \\ 31 & 32 & 33 & 34 & 35 & 36 & 37 & 38 & 39 & 30 \end{bmatrix} = \begin{bmatrix} 11 & 12 & 13 & 14 & 15 & 16 & 17 & 18 & 19 & 10 \\ 14 & 22 & 23 & 18 & 25 & 19 & 10 & 12 & 29 & 15 \\ 17 & 25 & 33 & 10 & 29 & 13 & 16 & 15 & 23 & 19 \end{bmatrix} \tag{46}$$

Generalization of Miller's rule to the case of the third-harmonic generation gives[29,30]

$$\delta_{ijk\ell}^{3\omega} = d_{ijk\ell}^{3\omega}/[\chi_{ii}(3\omega)\chi_{jj}\chi_{kk}\chi_{\ell\ell}] \quad . \tag{47}$$

Using equations (42), (43), and (44), we obtain

$$\begin{aligned} d_{11}^{3\omega} &= -b\gamma_1\chi_{xx}(3\omega)\chi_{xx}^3 \quad , \\ d_{12}^{3\omega} &= -b\gamma_6\chi_{xx}(3\omega)\chi_{yy}^3 \quad , \\ d_{13}^{3\omega} &= -b\gamma_8\chi_{xx}(3\omega)\chi_{zz}^3 \quad , \\ d_{14}^{3\omega} &= -b\gamma_4\chi_{xx}(3\omega)\chi_{xx}^2\chi_{yy} \quad , \quad \text{etc,} \end{aligned} \tag{48}$$

where $b = 1/N^3e^4$.

Note that an advantage of using the $d^{3\omega}$ rather than $\chi^{(3)}$ is that the factors of 3 and 6 which occur in equation (43) are eliminated.

Comparing the terms in (48) with equation (47) gives

$$\begin{aligned} &\delta_{11} = -b\gamma_1 \ , \quad \delta_{12} = -b\gamma_6 \ , \quad \delta_{13} = -b\gamma_8 \ , \quad \delta_{14} = -b\gamma_4 \ , \quad \delta_{15} = -b\gamma_{14} \ , \\ &\delta_{16} = -b\gamma_{11} \ , \quad \delta_{17} = -b\gamma_5 \ , \quad \delta_{18} = -b\gamma_{10} \ , \quad \delta_{19} = -b\gamma_{15} \ , \quad \delta_{10} = -b\gamma_{13} \ . \end{aligned} \tag{49}$$

When the results for the y_3'' and z_3'' solutions are included, one can express $\delta_{im}^{3\omega}$ in matrix form

[29] J. J. Wynne and G. D. Boyd, Study of Optical Difference Mixing in Ge and Si using a CO_2 Gas Laser, Appl. Phys. Lett. 12 (1968), 191.

[30] C. C. Wang, Empirical Relation Between the Linear and the Third-Order Nonlinear Optical Susceptibilities, Phys. Rev B2 (1970), 2045.

$$\delta_{im}^{3\omega} = -\frac{1}{e^4N^3}\begin{bmatrix} \gamma_1 & \gamma_6 & \gamma_8 & \gamma_4 & \gamma_{14} & \gamma_{11} & \gamma_5 & \gamma_{10} & \gamma_{15} & \gamma_{13} \\ \gamma_4 & \gamma_2 & \gamma_9 & \gamma_{10} & \gamma_7 & \gamma_{15} & \gamma_{13} & \gamma_6 & \gamma_{12} & \gamma_{14} \\ \gamma_5 & \gamma_7 & \gamma_3 & \gamma_{13} & \gamma_{12} & \gamma_8 & \gamma_{11} & \gamma_{14} & \gamma_9 & \gamma_{15} \end{bmatrix} . \qquad (50)$$

The reader should recall that this solution ignores the β contribution. The complete solution is given in the appendix and obeys the Kleinman condition given in equation (46).

7. CONCLUSIONS

We have derived the nonvanishing coefficients for optical doubling and tripling. The derivation is based on the Lorentz model where the linear response of the bound electrons to an incident electric field is described by a classical harmonic oscillator. Anharmonic terms (i.e., terms of higher order than quadratic in the potential) are added to describe the nonlinear response of the medium. These anharmonic terms are subject to the restriction that the potential remain invariant under the operations of each particular crystal class. The nonlinear optical constants $d_{ijk}^{2\omega}$ and $d_{ijk\ell}^{3\omega}$ were obtained, and the results were expressed in terms of Miller's δ's. Explicit expressions for the δ's are given in terms of the coefficients of the third- and fourth-degree polynomials of the potential. These coefficients were considered phenomenological, and no attempt was made to derive their values from a theoretical model.

Additional assumptions can be used to place further restrictions on the coefficients of the anharmonic terms in the potential. If we assume that the electrons contributing to the nonlinear susceptibilities are in a region relatively free of charge, then the potential obeys Laplace's equation, that is, $\nabla^2 U^{(n)} = 0$ for each n. This condition results in the following relations between the coefficients of the potential for n = 3:

$$\beta_1 + \beta_6 + \beta_8 = 0 , \quad \beta_2 + \beta_4 + \beta_9 = 0 , \quad \text{and } \beta_3 + \beta_5 + \beta_7 = 0 .$$

For the crystal classes C_6 and C6v, the condition

$$\beta_3 + \beta_5 + \beta_7 = 0 ,$$

when used in our results for Miller's $\delta_{ik}^{2\omega}$, requires that $2\delta_{31}^{2\omega} + \delta_{33}^{2\omega} = 0$. This result agrees with experimental data (within reported error) tabulated by Singh[6] for five of the seven values for the crystal class C_{6v}. Similarly, for n = 4, additional restrictions can be found for the γ_i's.

[6] S. Singh, Non-linear Optical Materials, in Handbook of Lasers, ed. by R. J. Pressley, The Chemical Rubber Co. (1971).

A number of authors have used quantum mechanics to derive expressions for the nonlinear coefficients (see Flytzanis,[7] for example); however, the usefulness of this approach has been limited by the inability to evaluate the required matrix elements. Although the classical anharmonic oscillator model has been applied to nonlinear optics by a number of authors, to our knowledge none has derived explicit expressions for the nonlinear coefficients in terms of the anharmonic coefficients for each crystal class. It should be possible to explicitly calculate the magnitude of β_i and γ_i, which would be useful in predicting new nonlinear materials. Work is in progress* in calculation of these coefficients using a point-charge model of crystal fields in an ionic solid.

ACKNOWLEDGEMENTS

The authors wish to thank our coworkers Richard P. Leavitt for his constant interest and invaluable suggestions, Frank Crowne for his helpful criticisms, and Herbert Dropkin for a critical reading of the manuscript. We are also grateful to Chi H. Lee from the University of Maryland for stimulating our original interest in this problem.

[7]C. Flytzanis, Theory of Nonlinear Optical Susceptibilities, in Quantum Electronics: A Treatise, Vol. 1, Nonlinear Optics, Part A, ed. by H. Robin and C. L. Tang, Academic Press, New York (1975).

*C. A. Morrison, Point charge model for the nonlinear optical coefficients in the anharmonic oscillator model, HDL internal report, in preparation.

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APPENDIX A.--SUMMARY OF RESULTS FOR ALL CRYSTAL CLASSES

The invariant polynomials, resultant potential, linear susceptibilities, and Miller's $\delta^{2\omega}$ and $\delta^{3\omega}$ are given according to crystal class. From $\delta^{2\omega}$, the second-harmonic-generation coefficients $d^{2\omega}$ can be constructed using equation (7) which we can rewrite as

$$d^{2\omega}_{ijk} = \delta^{2\omega}_{ijk}\chi_{ii}(2\omega)\chi_{jj}(\omega)\chi_{kk}(\omega) \quad .$$

Note that the appendix makes use of the contracted indices where the jk suffix of $\delta^{2\omega}_{ijk}$ is replaced by ℓ, where ℓ = 1, 2, 3, 4, 5, 6 replaces jk = 11, 22, 33, 23 (or 32), 13 (or 31), 12 (or 21), respectively. $\chi^{(2)}$ can be determined from $d^{2\omega}$ according to equation (4) in the body of the report, repeated here:

$$\chi^{(2)}_{i\ell} = d^{2\omega}_{i\ell} \text{ for } \ell \le 3 \text{ and } \chi^{(2)}_{i\ell} = 2d^{2\omega}_{i\ell} \text{ for } \ell \ge 4 \quad .$$

Similarly, the third-harmonic-generation coefficient $d^{3\omega}$ can be obtained from the $\delta^{3\omega}$ according to equation (47), which is rewritten as

$$d^{3\omega}_{ijk\ell} = \delta^{3\omega}_{ijk\ell}\chi_{ii}(3\omega)\chi_{jj}(\omega)\chi_{kk}(\omega)\chi_{\ell\ell}(\omega) \quad .$$

Again in the appendix we use the contracted indices δ_{im} where m replaces the jkℓ indices according to table 5 in the text. $\chi^{(3)}$ can then be determined from $d^{2\omega}$ according to $\chi^{(3)}_{im} = d^{3\omega}_{im}$ for $m \le 3$, $3d_{im}$ for $3 \le m \le 9$, and $6d_{im}$ for $m = 0$.

Crystal Class 1. C_1 (1)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_1

1. Invariant polynomials of second order:

$$x^2 \ , \quad y^2 \ , \quad z^2$$

2. Invariant polynomials of third order:

$$x^3, \ y^3, \ z^3, \ xy^2, \ xz^2, \ x^2y, \ x^2z, \ yz^2, \ y^2z, \ xyz$$

3. Invariant polynomials of fourth order:

$$x^4, \ y^4, \ z^4, \ x^3y, \ x^3z, \ xy^3, \ y^3z, \ xz^3, \ yz^3,$$

$$x^2y^2, \ x^2z^2, \ y^2z^2, \ x^2yz, \ xy^2z, \ xyz^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{3} \beta_1x^3 + \frac{1}{3} \beta_2y^3 + \frac{1}{3} \beta_3z^3 + \beta_4x^2y$$

$$+ \beta_5x^2z + \beta_6xy^2 + \beta_7y^2z + \beta_8xz^2 + \beta_9yz^2 + 2\beta_0xyz + \frac{1}{4} \gamma_1x^4$$

$$+ \frac{1}{4} \gamma_2y^4 + \frac{1}{4} \gamma_3z^4 + \gamma_4x^3y + \gamma_5x^3z + \gamma_6xy^3 + \gamma_7y^3z + \gamma_8xz^3$$

$$+ \gamma_9yz^3 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2 + 3\gamma_{13}x^2yz$$

$$+ 3\gamma_{14}xy^2z + 3\gamma_{15}xyz^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = Ne/D_y$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2} \begin{bmatrix} \beta_1 & \beta_6 & \beta_8 & \beta_0 & \beta_5 & \beta_4 \\ \beta_4 & \beta_2 & \beta_9 & \beta_7 & \beta_0 & \beta_6 \\ \beta_5 & \beta_7 & \beta_3 & \beta_9 & \beta_8 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4} [\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c] - \frac{1}{e^4N^3} G$$

where

$$B^a = \begin{bmatrix} \beta_1^2 & \beta_4\beta_6 & \beta_5\beta_8 & \beta_1\beta_4 & \frac{\beta_5\beta_6+2\beta_4\beta_0}{3} & \frac{\beta_1\beta_8+2\beta_5^2}{3} & \beta_1\beta_5 & \frac{\beta_1\beta_6+2\beta_4^2}{3} & \frac{\beta_4\beta_8+2\beta_5\beta_0}{3} & \frac{\beta_1\beta_0+2\beta_4\beta_5}{3} \\ \beta_1\beta_4 & \beta_6^2 & \beta_8\beta_0 & \frac{\beta_1\beta_6+2\beta_4^2}{3} & \beta_6\beta_0 & \frac{\beta_4\beta_8+2\beta_5\beta_0}{3} & \frac{\beta_1\beta_0+2\beta_4\beta_5}{3} & \beta_4\beta_6 & \frac{\beta_6\beta_8+2\beta_0^2}{3} & \frac{\beta_5\beta_6+2\beta_4\beta_0}{3} \\ \beta_1\beta_5 & \beta_6\beta_0 & \beta_8^2 & \frac{\beta_1\beta_0+2\beta_4\beta_5}{3} & \frac{\beta_6\beta_8+2\beta_0^2}{3} & \beta_5\beta_8 & \frac{\beta_1\beta_8+2\beta_5^2}{3} & \frac{\beta_5\beta_6+2\beta_4\beta_0}{3} & \beta_8\beta_0 & \frac{\beta_4\beta_8+2\beta_5\beta_0}{3} \end{bmatrix}$$

$$B^b = \begin{bmatrix} \beta_4^2 & \beta_2\beta_6 & \beta_9\beta_0 & \beta_4\beta_6 & \frac{\beta_2\beta_0+2\beta_6\beta_7}{3} & \frac{\beta_4\beta_9+2\beta_0^2}{3} & \beta_4\beta_0 & \frac{\beta_2\beta_4+2\beta_6^2}{3} & \frac{\beta_6\beta_9+2\beta_7\beta_0}{3} & \frac{\beta_4\beta_7+2\beta_6\beta_0}{3} \\ \beta_4\beta_6 & \beta_2^2 & \beta_7\beta_9 & \frac{\beta_2\beta_4+2\beta_6^2}{3} & \beta_2\beta_7 & \frac{\beta_6\beta_9+2\beta_7\beta_0}{3} & \frac{\beta_4\beta_7+2\beta_6\beta_0}{3} & \beta_2\beta_6 & \frac{\beta_2\beta_9+2\beta_7^2}{3} & \frac{\beta_2\beta_0+2\beta_6\beta_7}{3} \\ \beta_4\beta_0 & \beta_2\beta_7 & \beta_9^2 & \frac{\beta_4\beta_7+2\beta_6\beta_0}{3} & \frac{\beta_2\beta_9+2\beta_7^2}{3} & \beta_9\beta_0 & \frac{\beta_4\beta_9+2\beta_0^2}{3} & \frac{\beta_2\beta_0+2\beta_6\beta_7}{3} & \beta_7\beta_9 & \frac{\beta_6\beta_9+2\beta_7\beta_0}{3} \end{bmatrix}$$

$$B^c = \begin{bmatrix} \beta_5^2 & \beta_7\beta_0 & \beta_3\beta_8 & \beta_5\beta_0 & \frac{\beta_7\beta_8+2\beta_9\beta_0}{3} & \frac{\beta_3\beta_5+2\beta_8^2}{3} & \beta_5\beta_8 & \frac{\beta_5\beta_7+2\beta_0^2}{3} & \frac{\beta_3\beta_0+2\beta_8\beta_9}{3} & \frac{\beta_5\beta_9+2\beta_8\beta_0}{3} \\ \beta_5\beta_0 & \beta_7^2 & \beta_3\beta_9 & \frac{\beta_5\beta_7+2\beta_0^2}{3} & \beta_7\beta_9 & \frac{\beta_3\beta_0+2\beta_8\beta_9}{3} & \frac{\beta_5\beta_9+2\beta_8\beta_0}{3} & \beta_7\beta_0 & \frac{\beta_3\beta_7+2\beta_9^2}{3} & \frac{\beta_7\beta_8+2\beta_9\beta_0}{3} \\ \beta_5\beta_8 & \beta_7\beta_9 & \beta_3^2 & \frac{\beta_5\beta_9+2\beta_8\beta_0}{3} & \frac{\beta_3\beta_7+2\beta_9^2}{3} & \beta_3\beta_8 & \frac{\beta_3\beta_5+2\beta_8^2}{3} & \frac{\beta_7\beta_8+2\beta_9\beta_0}{3} & \beta_3\beta_9 & \frac{\beta_3\beta_0+2\beta_8\beta_9}{3} \end{bmatrix}$$

$$\Gamma = \begin{bmatrix} \gamma_1 & \gamma_6 & \gamma_8 & \gamma_4 & \gamma_{14} & \gamma_{11} & \gamma_5 & \gamma_{10} & \gamma_{15} & \gamma_{13} \\ \gamma_4 & \gamma_2 & \gamma_9 & \gamma_{10} & \gamma_7 & \gamma_{15} & \gamma_{13} & \gamma_6 & \gamma_{12} & \gamma_{14} \\ \gamma_5 & \gamma_7 & \gamma_3 & \gamma_{13} & \gamma_{12} & \gamma_8 & \gamma_{11} & \gamma_{14} & \gamma_9 & \gamma_{15} \end{bmatrix}$$

Crystal Class 2. C_i $(\bar{1})$

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_i

1. Invariant polynomials of second order:

$$x^2 \;,\quad y^2 \;,\quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$x^4,\; y^4,\; z^4,\; x^3y,\; x^3z,\; xy^3,\; y^3z,\; xz^3,\; yz^3,$$
$$x^2y^2,\; x^2z^2,\; y^2z^2,\; x^2yz,\; xy^2z,\; xyz^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4$$
$$+ \frac{1}{4} \gamma_3z^4 + \gamma_4x^3y + \gamma_5x^3z + \gamma_6xy^3 + \gamma_7y^3z + \gamma_8xz^3 + \gamma_9yz^3$$
$$+ \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2 + 3\gamma_{13}x^2yz + 3\gamma_{14}xy^2z$$
$$+ 3\gamma_{15}xyz^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4 N^3}\, G$$

where

$$B^a = B^b = B^c = 0$$

$$G = \begin{bmatrix} \gamma_1 & \gamma_5 & \gamma_6 & \gamma_4 & \gamma_{14} & \gamma_{11} & \gamma_5 & \gamma_{10} & \gamma_{15} & \gamma_{13} \\ \gamma_4 & \gamma_2 & \gamma_9 & \gamma_{10} & \gamma_7 & \gamma_{15} & \gamma_{13} & \gamma_6 & \gamma_{12} & \gamma_{14} \\ \gamma_5 & \gamma_7 & \gamma_3 & \gamma_{13} & \gamma_{12} & \gamma_8 & \gamma_{11} & \gamma_{14} & \gamma_9 & \gamma_{15} \end{bmatrix}$$

Crystal Class 3. C_2 (2)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_2

1. Invariant polynomials of second order:

$$x^2 \quad , \quad y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$z^3, \quad x^2z, \quad y^2z, \quad xyz$$

3. Invariant polynomials of fourth order:

$$x^4, \quad y^4, \quad z^4, \quad x^3y \ , \quad xy^3, \quad x^2y^2, \quad x^2z^2, \quad y^2z^2, \quad xyz^2$$

4. *Potential energy:*

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{3} \beta_3z^3 + \beta_5x^2z$$

$$+ \beta_7y^2z + 2\beta_0xyz + \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4 + \frac{1}{4} \gamma_3z^4 + \gamma_4x^3y$$

$$+ \gamma_6xy^3 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2$$

$$+ 3\gamma_{15}xyz^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = Ne/D_y$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & \beta_0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_7 & \beta_0 & 0 \\ \beta_5 & \beta_7 & \beta_3 & 0 & 0 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3} G$$

where

$$B^a = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & 0 & \frac{2B_5B_0}{3} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{2B_5B_0}{3} & 0 & 0 & \frac{2B_0^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & \frac{2B_5^2}{3} & 0 & 0 & \frac{2B_5B_0}{3} \end{bmatrix}$$

$$B^b = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & \frac{2B_7B_0}{3} & \\ 0 & 0 & 0 & 0 & 0 & \frac{2B_7B_0}{3} & 0 & 0 & \frac{2B_7^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_7^2}{3} & 0 & \frac{2B_0^2}{3} & 0 & 0 & \frac{2B_7B_0}{3} \end{bmatrix}$$

$$B^c = \begin{bmatrix} B_5^2 & B_7B_0 & 0 & B_5B_0 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_5B_7+2B_0^2}{3} & \frac{B_3B_0}{3} & 0 \\ B_5B_0 & B_7^2 & 0 & \frac{B_5B_7+2B_0^2}{3} & 0 & \frac{B_3B_0}{3} & 0 & B_7B_0 & \frac{B_3B_7}{3} & 0 \\ 0 & 0 & B_3^2 & 0 & \frac{B_3B_7}{3} & 0 & \frac{B_3B_5}{3} & 0 & 0 & \frac{B_3B_0}{3} \end{bmatrix}$$

$$\Gamma = \begin{bmatrix} \gamma_1 & \gamma_6 & 0 & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & \gamma_{15} & 0 \\ \gamma_4 & \gamma_2 & 0 & \gamma_{10} & 0 & \gamma_{15} & 0 & \gamma_6 & \gamma_{12} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{12} & 0 & \gamma_{11} & 0 & 0 & \gamma_{15} \end{bmatrix}$$

Crystal Class 4. C_s (m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS C_s

1. Invariant polynomials of second order:

$$x^2 \quad , \quad y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$x^3 \quad , \quad y^3 \quad , \quad xy^2 \quad , \quad xz^2 \quad , \quad x^2y \quad , \quad yz^2$$

3. Invariant polynomials of fourth order:

$$x^4 \quad , \quad y^4 \quad , \quad z^4 \quad , \quad x^3y \quad , \quad xy^3 \quad , \quad x^2y^2 \quad , \quad x^2z^2 \quad , \quad y^2z^2 \quad , \quad xyz^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{3} \beta_1x^3 + \frac{1}{3} \beta_2y^3 + \beta_4x^2y$$
$$+ \beta_6xy^2 + \beta_8xz^2 + \beta_9yz^2 + \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4 + \frac{1}{4} \gamma_3z^4 + \gamma_4x^3y$$
$$+ \gamma_6xy^3 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2 + 3\gamma_{15}xyz^2$$

5. Linear Susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} \beta_1 & \beta_6 & \beta_8 & 0 & 0 & \beta_4 \\ \beta_4 & \beta_2 & \beta_9 & 0 & 0 & \beta_6 \\ 0 & 0 & 0 & \beta_9 & \beta_8 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3} G$$

where

$$
B^{1} = \begin{bmatrix}
B_1^2 & B_4B_{[illegible]} & [illegible] & B_1B_4 & 0 & \frac{B_1B_8}{3} & 0 & \frac{B_1B_6+2B_4^2}{3} & \frac{B_4B_8}{3} & 0 \\
B_1B_4 & B_{[illegible]}^2 & [illegible] & \frac{B_1B_{[illegible]}+2B_4^2}{3} & 0 & \frac{B_4B_8}{3} & 0 & B_4B_6 & \frac{B_6B_8}{3} & 0 \\
[illegible] & [illegible] & B_{[illegible]}^2 & 0 & \frac{B_6B_8}{3} & 0 & \frac{B_1B_3}{3} & 0 & 0 & \frac{B_4B_8}{3}
\end{bmatrix}
$$

$$
B^{2} = \begin{bmatrix}
B_4^2 & [illegible] & [illegible] & B_4B_{[illegible]} & 0 & \frac{B_4B_4}{3} & 0 & \frac{B_2B_4+2B_6^2}{3} & \frac{B_6B_9}{3} & 0 \\
B_4B_6 & B_{[illegible]}^2 & 0 & \frac{B_2B_4+2B_6^2}{3} & 0 & \frac{B_6B_{[illegible]}}{3} & 0 & B_2B_6 & \frac{B_2B_9}{3} & 0 \\
[illegible] & [illegible] & B_9^2 & 0 & \frac{B_{[illegible]}B_{[illegible]}}{3} & 0 & \frac{B_4B_9}{3} & 0 & 0 & \frac{B_6B_9}{3}
\end{bmatrix}
$$

$$
B^{3} = \begin{bmatrix}
0 & [illegible] & 0 & [illegible] & 0 & \frac{4B_{[illegible]}^2}{[illegible]} & 0 & 0 & \frac{2B_8B_9}{3} & 0 \\
[illegible] & [illegible] & 0 & 0 & [illegible] & \frac{2B_{[illegible]}B_9}{3} & 0 & 0 & \frac{2B_4^2}{3} & 0 \\
[illegible] & [illegible] & [illegible] & 0 & \frac{2B_4^2}{3} & 0 & \frac{2B_9^2}{3} & 0 & [illegible] & \frac{2B_8B_9}{3}
\end{bmatrix}
$$

$$
\Gamma = \begin{bmatrix}
\gamma_1 & \gamma_6 & [illegible] & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & \gamma_{15} & 0 \\
\gamma_4 & \gamma_{[illegible]} & 0 & \gamma_{10} & 0 & \gamma_{15} & 0 & \gamma_6 & \gamma_{12} & 0 \\
[illegible] & [illegible] & \gamma_3 & 0 & \gamma_{12} & 0 & \gamma_{11} & 0 & 0 & \gamma_{15}
\end{bmatrix}
$$

Crystal Class 5. C_{2h} (2/m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_{2h}

1. Invariant polynomials of second order:

$$x^2 \quad , \quad y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$x^4 \ , \ y^4 \ , \ z^4 \ , \ x^3y \ , \ xy^3 \ , \ x^2y^2 \ , \ x^2z^2 \ ,$$
$$y^2z^2 \ , \ xyz^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4$$
$$+ \frac{1}{4} \gamma_3z^4 + \gamma_4x^3y + \gamma_6xy^3 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2$$
$$+ \frac{3}{2} \gamma_{12}y^2z^2 + 3\gamma_{15}xyz^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$.

$$\delta^{3\omega} = \frac{1}{e^6N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3}\, G$$

where

$B^a = B^b = B^c = 0$

$$G = \begin{bmatrix} \gamma_1 & \gamma_6 & 0 & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & \gamma_{15} & 0 \\ \gamma_4 & \gamma_2 & 0 & \gamma_{10} & 0 & \gamma_{15} & 0 & \gamma_6 & \gamma_{12} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{12} & 0 & \gamma_{11} & 0 & 0 & \gamma_{15} \end{bmatrix}$$

Crystal Class 6. D_2 (222)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_2

1. Invariant polynomials of second order:

$$x^2 \quad , \quad y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$xyz$$

3. Invariant polynomials of fourth order:

$$x^4 \quad , \quad y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad x^2z^2 \quad , \quad y^2z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + 2\beta_0 xyz + \frac{1}{4} \gamma_1 x^4$$
$$+ \frac{1}{4} \gamma_2 y^4 + \frac{1}{4} \gamma_3 z^4 + \frac{3}{2} \gamma_{10} x^2y^2 + \frac{3}{2} \gamma_{11} x^2z^2 + \frac{3}{2} \gamma_{12} y^2z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2} \begin{bmatrix} 0 & 0 & 0 & \beta_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4} \left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3} G$$

where

$$
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 \\
0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
$$

$$
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0
\end{bmatrix}
$$

$$
\begin{bmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 \\
0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
$$

$$
\begin{bmatrix}
[illegible] & & & [illegible] & [illegible] & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\
 & [illegible] & & [illegible] & 0 & 0 & 0 & 0 & \gamma_{12} & 0 \\
 & & [illegible] & & [illegible] & & \gamma_{11} & 0 & 0 & 0
\end{bmatrix}
$$

Crystal Class 7. C_{2v} (mm)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS C_{2v}

1. Invariant polynomials of second order:

$$x^2 \;,\quad y^2 \;,\quad z^2$$

2. Invariant polynomials of third order:

$$z^3 \;,\quad x^2z \;,\quad y^2z$$

3. Invariant polynomials of fourth order:

$$x^4 \;,\quad y^4 \;,\quad z^4 \;,\quad x^2y^2 \;,\quad x^2z^2 \;,\quad y^2z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{3} \beta_3z^3 + \beta_5x^2z + \beta_7y^2z$$
$$+ \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4 + \frac{1}{4} \gamma_3z^4 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & 0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_7 & 0 & 0 \\ \beta_5 & \beta_7 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3} G$$

where

$$B^a = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$B^b = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_7^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_7^2}{3} & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$B^c = \begin{bmatrix} B_5^2 & 0 & 0 & 0 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_5B_7}{3} & 0 & 0 \\ 0 & B_7^2 & 0 & \frac{B_5B_7}{3} & 0 & 0 & 0 & 0 & \frac{B_3B_7}{3} & 0 \\ 0 & 0 & B_3^2 & 0 & \frac{B_3B_7}{3} & 0 & \frac{B_3B_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_2 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{12} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{12} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 8. D_{2h} (mmm)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_{2h}

1. Invariant polynomials of second order:

$$x^2 \quad , \quad y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$x^4 \quad , \quad y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad x^2z^2 \quad , \quad y^2z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2x^2 + \frac{1}{2} m_y\omega_y^2y^2 + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{4} \gamma_1x^4 + \frac{1}{4} \gamma_2y^4$$
$$+ \frac{1}{4} \gamma_3z^4 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}x^2z^2 + \frac{3}{2} \gamma_{12}y^2z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = Ne/D_y$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^a + \chi_{yy}(2\omega)B^b + \chi_{zz}(2\omega)B^c\right] - \frac{1}{e^4N^3}\,G$$

where

$B^a = B^b = B^c = 0$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_2 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{12} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{12} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 9. C_4 (4)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_4

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$z^3 \quad , \quad (x^2 + y^2)z$$

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2 \quad , \quad (x^2 - y^2)xy$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{3} \beta_3 z^3 + \beta_5(x^2 + y^2)z$$
$$+ \frac{1}{4} \gamma_1(x^4 + y^4) + \frac{1}{4} \gamma_3 z^4 + \gamma_4(x^2 - y^2)xy + \frac{3}{2} \gamma_{10}x^2y^2$$
$$+ \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & 0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_5 & 0 & 0 \\ \beta_5 & \beta_5 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}G$$

where

$$B^{ab} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} B_5^2 & 0 & 0 & 0 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_5^2}{3} & 0 & 0 \\ 0 & B_5^2 & 0 & \frac{B_5^2}{3} & 0 & 0 & 0 & 0 & \frac{B_3B_5}{3} & 0 \\ 0 & 0 & B_3^2 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_3B_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & -\gamma_4 & 0 & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ \gamma_4 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & -\gamma_4 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 10. S_4 ($\bar{4}$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS S_4

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$(x^2 - y^2)z \quad , \quad xyz$$

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2 \quad , \quad (x^2 - y^2)xy$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2z^2 + \beta_5(x^2 - y^2)z + 2\beta_0 xyz$$
$$+ \frac{1}{4}\gamma_1(x^4 + y^4) + \frac{1}{4}\gamma_3 z^4 + \gamma_4(x^2 - y^2)xy + \frac{3}{2}\gamma_{10}x^2y^2$$
$$+ \frac{3}{2}\gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & \beta_0 & \beta_5 & 0 \\ 0 & 0 & 0 & -\beta_5 & \beta_0 & 0 \\ \beta_5 & -\beta_5 & 0 & 0 & 0 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}G$$

where

$$B^{ab} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2(B_0^2+B_5^2)}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2(B_0^2+B_5^2)}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2(B_0^2+B_5^2)}{3} & 0 & \frac{2(B_0^2+B_5^2)}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} B_5^2 & -B_5B_0 & 0 & B_5B_0 & 0 & 0 & 0 & \frac{2B_0^2-B_5^2}{3} & 0 & 0 \\ B_5B_0 & B_5^2 & 0 & \frac{2B_0^2-B_5^2}{3} & 0 & 0 & 0 & -B_5B_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & -\gamma_4 & 0 & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ \gamma_4 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & -\gamma_4 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 11. C_{4h} (4/m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS C_{4h} (4/m)

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Irvariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2 \quad , \quad (x^2 - y^2)xy$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{4} \gamma_1(x^4 + y^4) + \frac{1}{4} \gamma_3 z^4$$

$$+ \gamma_4(x^2 - y^2)xy + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}\,G$$

where

$$B^{ab} = B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & -\gamma_4 & 0 & \gamma_4 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ \gamma_4 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & -\gamma_4 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 12. D_4 (422)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS D_4

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{4} \gamma_1(x^4 + y^4) + \frac{1}{4} \gamma_3 z^4$$
$$+ \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\,G$$

where

$$B^{ab} = B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 13. C_{4v} (4mm)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_{4v}

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$z^3 \quad , \quad (x^2 + y^2)z$$

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2z^2 + \frac{1}{3} \beta_3z^3 + \beta_5(x^2 + y^2)z$$

$$+ \frac{1}{4} \gamma_1(x^4 + y^4) + \frac{1}{4} \gamma_3z^4 + \frac{3}{2} \gamma_{10}x^2y^2 + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & 0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_5 & 0 & 0 \\ \beta_5 & \beta_5 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}\,G$$

where

$$B^{ab} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_5^2}{3} & 0 & \frac{2B_5^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} B_5^2 & 0 & 0 & 0 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_5^2}{3} & 0 & 0 \\ 0 & B_5^2 & 0 & \frac{B_5^2}{3} & 0 & 0 & 0 & 0 & \frac{B_3B_5}{3} & 0 \\ 0 & 0 & B_3^2 & 0 & \frac{B_3B_5}{3} & 0 & \frac{B_3B_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 14. D_{2d} ($\bar{4}2m$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_{2d}

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$xyz$$

3. Invariant polynomials of fourth order:

$$x^4 + y^4 \quad , \quad z^4 \quad , \quad x^2y^2 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \beta_0 xyz + \frac{1}{4} \gamma_1(x^4 + y^4)$$
$$+ \frac{1}{4} \gamma_3 z^4 + \frac{3}{2} \gamma_{10} x^2y^2 + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & \beta_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\, G$$

where

$$B^{ab} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 \\ 0 & 0 & 0 & \frac{2B_0^2}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

APPENDIX A: D_{4h}

Crystal Class 15. D_{4h} (4/mmm)

INVARIANT POLYNOMIALS, *LINEAR SUSCEPTIBILITIES*, AND MILLER'S δ FOR CRYSTAL CLASS D_{4h}

Same as for crystal class 12, D_4

Crystal Class 16. C_3 (3)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_3

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$x^3 - 3xy^2 \quad , \quad y^3 - 3yx^2 \quad , \quad z^3 \quad , \quad (x^2 + y^2)z$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \quad , \quad (x^3 - 3xy^2)z \quad , \quad (y^3 - 3x^2y)z \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{3} \beta_1(x^3 - 3xy^2)$$
$$+ \frac{1}{3} \beta_2(y^3 - 3x^2y) + \frac{1}{3} \beta_3 z^3 + \beta_5(x^2 + y^2)z$$
$$+ \frac{1}{4} \gamma_1(x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4 + \gamma_5(x^3 - 3xy^2)z$$
$$+ \gamma_7(y^3 - 3x^2y)z + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} \beta_1 & -\beta_1 & 0 & 0 & \beta_5 & -\beta_2 \\ -\beta_2 & \beta_2 & 0 & \beta_5 & 0 & -\beta_1 \\ \beta_5 & \beta_5 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3} G$$

where

$$B^{ab} = \begin{bmatrix} \beta_1^2+\beta_2^2 & 0 & 0 & 0 & -\beta_1\beta_5 & \frac{2\beta_5^2}{3} & \beta_1\beta_5 & \frac{\beta_1^2+\beta_2^2}{3} & 0 & -\beta_2\beta_5 \\ 0 & \beta_1^2+\beta_2^2 & 0 & \frac{\beta_1^2+\beta_2^2}{3} & \beta_2\beta_5 & 0 & -\beta_2\beta_5 & 0 & \frac{2\beta_5^2}{3} & -\beta_1\beta_5 \\ \beta_1\beta_5 & \beta_2\beta_5 & 0 & -\beta_2\beta_5 & \frac{2\beta_5^2}{3} & 0 & \frac{2\beta_5^2}{3} & -\beta_1\beta_5 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} \beta_5^2 & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_5^2}{3} & 0 & 0 \\ 0 & \beta_5^2 & 0 & \frac{\beta_5^2}{3} & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 \\ 0 & 0 & \beta_3^2 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_3\beta_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & -\gamma_5 & \gamma_{11} & \gamma_5 & \frac{\gamma_1}{3} & 0 & -\gamma_7 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & \gamma_7 & 0 & -\gamma_7 & 0 & \gamma_{11} & -\gamma_5 \\ \gamma_5 & \gamma_7 & \gamma_3 & -\gamma_7 & \gamma_{11} & 0 & \gamma_{11} & -\gamma_5 & 0 & 0 \end{bmatrix}$$

Crystal Class 17. C_{3i}, S_6 ($\bar{3}$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_{3i}

1. Invariant polynomials of second order:

$$x^2 + y^2 , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 , \quad z^4 , \quad (x^3 - 3xy^2)z , \quad (y^3 - 3x^2y)z ,$$
$$(x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{4} \gamma_1(x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4$$
$$+ \gamma_5(x^3 - 3xy^2)z + \gamma_7(y^3 - 3x^2y)z + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$
$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$
$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\, G$$

where

$$B^{ab} = B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & -\gamma_5 & \gamma_{11} & \gamma_5 & \frac{\gamma_1}{3} & 0 & -\gamma_7 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & \gamma_7 & 0 & -\gamma_7 & 0 & \gamma_{11} & -\gamma_5 \\ \gamma_5 & \gamma_7 & \gamma_3 & -\gamma_7 & \gamma_{11} & 0 & \gamma_{11} & -\gamma_5 & 0 & 0 \end{bmatrix}$$

Crystal Class 18. D_3 (32)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS D_3

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$y^3 - 3yx^2$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \; , \quad (x^3 - 3xy^2)z \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 + \frac{1}{3} \beta_2 (y^3 - 3x^2 y)$$

$$+ \frac{1}{4} \gamma_1 (x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4 + \gamma_5 (x^3 - 3xy^2) z$$

$$+ \frac{3}{2} \gamma_{11} (x^2 + y^2) z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3 N^2} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -\beta_2 \\ -\beta_2 & \beta_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\,G$$

where

$$B^{ab} = \begin{bmatrix} B_2^2 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{B_2^2}{3} & 0 & 0 \\ 0 & B_2^2 & 0 & \frac{B_2^2}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & -\gamma_5 & \gamma_{11} & \gamma_5 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & -\gamma_5 \\ \gamma_5 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & -\gamma_5 & 0 & 0 \end{bmatrix}$$

Crystal Class 19. C_{3v} (3m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_{3v}

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$x^3 - 3xy^2 \quad , \quad z^3 \quad , \quad (x^2 + y^2)z$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \quad , \quad (x^3 - 3xy^2)z \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{3} \beta_1(x^3 - 3xy^2)$$

$$+ \frac{1}{3} \beta_3 z^3 + \beta_5(x^2 + y^2)z + \frac{1}{4} \gamma_1(x^2 + y^2)^2$$

$$+ \frac{1}{4} \gamma_3 z^4 + \gamma_5(x^3 - 3xy^2)z + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} \beta_1 & -\beta_1 & 0 & 0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_5 & 0 & -\beta_1 \\ \beta_5 & \beta_5 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}\,G$$

where

$$B^{ab} = \begin{bmatrix} \beta_1^2 & 0 & 0 & 0 & -\beta_1\beta_5 & \frac{2\beta_5^2}{3} & \beta_1\beta_5 & \frac{\beta_1^2}{3} & 0 & 0 \\ 0 & \beta_1^2 & 0 & \frac{\beta_1^2}{3} & 0 & 0 & 0 & 0 & \frac{2\beta_5^2}{3} & -\beta_1\beta_5 \\ \beta_1\beta_5 & 0 & 0 & 0 & \frac{2\beta_5^2}{3} & 0 & \frac{2\beta_5^2}{3} & -\beta_1\beta_5 & 0 & 0 \end{bmatrix}$$

$$B^{c} = \begin{bmatrix} \beta_5^2 & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_5^2}{3} & 0 & 0 \\ 0 & \beta_5^2 & 0 & \frac{\beta_5^2}{3} & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 \\ 0 & 0 & \beta_3^2 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_3\beta_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & -\gamma_5 & \gamma_{11} & \gamma_5 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & -\gamma_5 \\ \gamma_5 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & -\gamma_5 & 0 & 0 \end{bmatrix}$$

Crystal Class 20. D_{3d} ($\bar{3}m$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_{3d}

1. Invariant polynomials of second order:

$$x^2 + y^2 , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 , \quad z^4 , \quad (x^3 - 3xy^2)z , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 + \frac{1}{4} \gamma_1 (x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4$$

$$+ \gamma_5 (x^3 - 3xy^2)z + \frac{3}{2} \gamma_{11} (x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\, G$$

where

$$B^{ab} = B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & -\gamma_5 & \gamma_{11} & \gamma_5 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & -\gamma_5 \\ \gamma_5 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & -\gamma_5 & 0 & 0 \end{bmatrix}$$

Crystal Class 21. C_6 (6)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_6

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$z^3 \quad , \quad (x^2 + y^2)z$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2) + \frac{1}{2} m_z\omega_z^2 z^2 + \frac{1}{3} \beta_3 z^3 + \beta_5(x^2 + y^2)z$$

$$+ \frac{1}{4} \gamma_1(x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4 + \frac{3}{2} \gamma_{11}(x^2 + y^2)z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & 0 & \beta_5 & 0 \\ 0 & 0 & 0 & \beta_5 & 0 & 0 \\ \beta_5 & \beta_5 & \beta_3 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3}\,G$$

where

$$B^{ab} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2\beta_5^2}{3} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2\beta_5^2}{3} & 0 \\ 0 & 0 & 0 & 0 & \frac{2\beta_5^2}{3} & 0 & \frac{2\beta_5^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$= \begin{bmatrix} \beta_5^2 & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_5^2}{3} & 0 & 0 \\ 0 & \beta_5^2 & 0 & \frac{\beta_5^2}{3} & 0 & 0 & 0 & 0 & \frac{\beta_3\beta_5}{3} & 0 \\ 0 & 0 & \beta_3^2 & 0 & \frac{\beta_3\beta_5}{3} & 0 & \frac{\beta_3\beta_5}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 22. C_{3h} $(\bar{6})$

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS C_{3h}

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$x^3 - 3xy^2 \quad , \quad y^3 - 3yx^2$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 + \frac{1}{3} \beta_1 (x^3 - 3xy^2)$$

$$+ \frac{1}{3} \beta_2 (y^3 - 3x^2 y) + \frac{1}{4} \gamma_1 (x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4$$

$$+ \frac{3}{2} \gamma_{11} (x^2 + y^2) z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3 N^2} \begin{bmatrix} \beta_1 & -\beta_1 & 0 & 0 & 0 & -\beta_2 \\ -\beta_2 & \beta_2 & 0 & 0 & 0 & -\beta_1 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}G$$

where

$$B^{ab} = \begin{bmatrix} B_1^2+B_2^2 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{B_1^2+B_2^2}{3} & 0 & 0 \\ 0 & B_1^2+B_2^2 & 0 & \frac{B_1^2+B_2^2}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$B^c = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 23. C_{6h} (6/m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS C_{6h}

1. Invariant polynomials of second order:

$$x^2 + y^2 , \quad z^2$$

2. Invariant polynomials of third order:

none

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 , \quad z^4 , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 + \frac{1}{4} \gamma_1 (x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4$$

$$+ \frac{3}{2} \gamma_{11} (x^2 + y^2) z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4N^3}\,G$$

where

$B^{ab} = B^{c} = 0$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 24. D_6 (622)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS D_6

Same as for crystal class 23, C_{6h}

Crystal Class 25. C_{6v} (6mm)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS C_{6v}

Same as for crystal class 21, C_6

Crystal Class 26. D_{3h} ($\bar{6}m2$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_{3h}

1. Invariant polynomials of second order:

$$x^2 + y^2 \quad , \quad z^2$$

2. Invariant polynomials of third order:

$$y^3 - 3yx^2$$

3. Invariant polynomials of fourth order:

$$(x^2 + y^2)^2 \quad , \quad z^4 \quad , \quad (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2) + \frac{1}{2} m_z \omega_z^2 z^2 + \frac{1}{3} \beta_2 (y^3 - 3x^2 y)$$

$$+ \frac{1}{4} \gamma_1 (x^2 + y^2)^2 + \frac{1}{4} \gamma_3 z^4 + \frac{3}{2} \gamma_{11} (x^2 + y^2) z^2$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = Ne/D_x$$

$$\chi_{yy}(\omega) = \chi_{xx}(\omega)$$

$$\chi_{zz}(\omega) = Ne/D_z$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3 N^2} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & -\beta_2 \\ -\beta_2 & \beta_2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{ab} + \chi_{zz}(2\omega)B^{c}\right] - \frac{1}{e^4 N^3} G$$

where

$$B^{ab} = \begin{bmatrix} \beta_2^2 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\beta_2^2}{3} & 0 & 0 \\ 0 & \beta_2^2 & 0 & \frac{\beta_2^2}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

$$B^{c} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{11} & 0 & \frac{\gamma_1}{3} & 0 & 0 \\ 0 & \gamma_1 & 0 & \frac{\gamma_1}{3} & 0 & 0 & 0 & 0 & \gamma_{11} & 0 \\ 0 & 0 & \gamma_3 & 0 & \gamma_{11} & 0 & \gamma_{11} & 0 & 0 & 0 \end{bmatrix}$$

APPENDIX A: D_{6h}

Crystal Class 27. D_{6h} (6/mmm)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS D_{6h}

Same as for crystal class 23, C_{6h}

Crystal Class 28. T (23)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS T

1. Invariant polynomials of second order:

$$x^2 + y^2 + z^2$$

2. Invariant polynomials of tnird order:

$$xyz$$

3. Invariant polynomials of fourth order:

$$x^4 + y^4 + z^4 \quad , \quad x^2y^2 + x^2z^2 + y^2z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x\omega_x^2(x^2 + y^2 + z^2) + 2\beta_0 xyz + \frac{1}{4} \gamma_1 (x^4 + y^4 + z^4)$$
$$+ \frac{3}{2} \gamma_{10}(x^2y^2 + x^2z^2 + y^2z^2)$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = \chi_{yy}(\omega) = \chi_{zz}(\omega) = Ne/D_x$$

where $D_i(\omega) = (\omega_i^2 - \omega^2)m_i/e$.

6. Miller's $\delta^{2\omega}$:

$$\delta^{2\omega} = \frac{1}{e^3N^2}\begin{bmatrix} 0 & 0 & 0 & \beta_0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \beta_0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \beta_0 \end{bmatrix}$$

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4} \left[\chi_{xx}(2\omega) B^{abc} \right] - \frac{1}{e^4 N^3} G$$

where

$$B^{abc} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & \frac{2\beta_0^2}{3} & 0 & \frac{2\beta_0^2}{3} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2\beta_0^2}{3} & 0 \\ 0 & 0 & 0 & \frac{2\beta_0^2}{3} & \frac{2\beta_0^2}{3} & 0 & \frac{2\beta_0^2}{3} & 0 & 0 & 0 \end{bmatrix}$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{10} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{10} & 0 \\ 0 & 0 & \gamma_1 & 0 & \gamma_{10} & 0 & \gamma_{10} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 29. T_h (m3)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES, AND MILLER'S δ FOR CRYSTAL CLASS T_h

1. Invariant polynomials of second order:

$$x^2 + y^2 + z^2$$

2. Invariant polynomials of third order:

none

3. *Invariant polynomials of fourth order:*

$$x^4 + y^4 + z^4 \quad , \quad x^2y^2 + (x^2 + y^2)z^2$$

4. Potential energy:

$$U = \frac{1}{2} m_x \omega_x^2 (x^2 + y^2 + z^2) + \frac{1}{4} \gamma_1 (x^4 + y^4 + z^4)$$

$$+ \frac{3}{2} \gamma_{10} (x^2y^2 + x^2z^2 + y^2z^2)$$

5. Linear susceptibilities:

$$\chi_{xx}(\omega) = \chi_{yy}(\omega) = \chi_{zz}(\omega) = Ne/D_x$$

where $D_i(\omega) = (\omega_i^2 - \omega^2) m_i / e$.

6. Miller's $\delta^{2\omega}$:

none

7. Miller's $\delta^{3\omega}$:

$$\delta^{3\omega} = \frac{2}{e^6 N^4}\left[\chi_{xx}(2\omega)B^{abc}\right] - \frac{1}{e^4 N^3}\,G$$

where

$$B^{abc} = 0$$

$$G = \begin{bmatrix} \gamma_1 & 0 & 0 & 0 & 0 & \gamma_{10} & 0 & \gamma_{10} & 0 & 0 \\ 0 & \gamma_1 & 0 & \gamma_{10} & 0 & 0 & 0 & 0 & \gamma_{10} & 0 \\ 0 & 0 & \gamma_1 & 0 & \gamma_{10} & 0 & \gamma_{10} & 0 & 0 & 0 \end{bmatrix}$$

Crystal Class 30. O (432)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS O

Same as for crystal class 29, T_h

Crystal Class 31. T_d ($\bar{4}3m$)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS T_d

Same as for crystal class 28, T

Crystal Class 32. O_h (m3m)

INVARIANT POLYNOMIALS, LINEAR SUSCEPTIBILITIES,
AND MILLER'S δ FOR CRYSTAL CLASS O_h

Same as for crystal class 30, O

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